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Optimization of biodiesel production from soybean oil in a microreactor

Masoud Rahimi [a,b,*], Babak Aghel [a], Mohammad Alitabar [b], Arash Sepahvand [b], Hamid Reza Ghasempour [b]

[a] CFD Research Center, Chemical Engineering Department, Razi University, Kermanshah, Iran
[b] Department of Biotechnology–Chemical Engineering, Science and Research Branch, Islamic Azad University, Kermanshah, Iran

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ABSTRACT

Transesterification of soybean oil with methanol in the presence of potassium hydroxide, as a catalyst, in a microreactor has been investigated. The transesterification reaction was performed at specific condition in circular tubes with hydraulic diameter of (0.8 mm). In order to further improve the biodiesel production, the experimental design was performed using Box–Behnken method. The results were analyzed using response surface methodology. The influence of reaction variables including; molar ratio of methanol to oil (6:1–12:1), temperature (55–65 °C) and catalyst concentration (0.6–1.8 wt.%) and residence time (20–180 s) under various flow rates of reactants (1–11 ml min^{-1}) on Fatty Acid Methyl Ester (FAME) transesterification reaction was studied. The optimum condition was found at molar ratio of methanol to oil (9:1), catalyst concentration (1.2 wt.%) and temperature (60 °C) with a FAME % of about 89%. Considering optimum parameters, by changing the reactant residence time the FAME % was reached to 98% at 180 s.

1. Introduction

The limited fossil fuel resources along with the need of reduce green house gases emissions were major impulses to the development of alternative fuels. As a result, increased attention has been given to biofuels, such as biodiesel, which can be used as an alternative fuel in compression–ignition engines [1]. The other advantage of biofuels is its contribution to reduce of CO_2 emissions; because of it comprises a closed carbon cycle [2,3]. Biodiesel produced by transesterification of renewable resources, such as vegetable oils and animal fats with monohydric alcohol, which is commonly methanol, makes it biodegradable and nontoxic [4]. The transesterification reaction is three-step reversible reaction for converting the triglyceride into a mixture of esters (biodiesel) and glycerol in the presence of a catalyst. During transesterification reaction, the triglyceride is converted to the diglyceride, monoglyceride and glycerol in the three steps, and one mol of ester produces at each step.

Two types of catalysts including; homogeneous (acid or base) and heterogeneous (acid, base, and enzymatic) were used for transesterification of vegetable oils [5–8]. Biodiesel has some disadvantages such as high feedstock cost, energy requirements, residence time, lower volumetric energy content and low-temperature operability [9,10]. Commonly, biodiesel is produced with batch reactors at a residence time that may take from one hour to several hours [11,12]. Due to the high residence time, many research focused on reducing process time and promote the efficiency of the biodiesel process [13,14]. Hanh et al. [15] investigated transesterification of methyl esters in presence of 40 kHz ultrasonic irradiation at room temperature. Microwave method to provide biodiesel using action ion-exchange resin particles (CERP)/PES catalytic was assisted by Zhang et al. [16]. They showed that at the optimal conditions, this method is a fast and easy way for producing biodiesel with a reaction time of 90 min. Among other methods, in a study done by Yin et al. [17], supercritical transesterification of soybean oil with co-solvent attained methyl ester yield of more than 98% during 10 min at temperature of 350 °C. They found that by adding hexane as co-solvent to carbon dioxide at 300 °C, the yield of methyl ester was notably increased. From the literature, continuous transesterification of oils with catalyst to improve the efficiency were proposed by many researchers [18–20].

It is known that the main drawback of base-catalyzed biodiesel process is high cost and time consumed during transesterification and disposal of large amount of waste water. The cost of operation will be decreased if the time of process decreases. In order to increase the conversion efficiency of biodiesel under continuous condition, microreactor can be used. Microchannel reactor as a continuous reactor has many advantages such as high volume/surface ratio, higher transport (e.g., heat and mass transfer) rates, short diffusion distance, simplify process control and so on used in the industrial process [21]. Sun et al. [22] used a microstructure reactor with a 0.6 mm stainless steel capillary diameter for transesterification of cotton seed oil with methanol. They evaluated many parameters on transesterification and reached the best yield of methyl ester at 120 °C with a residence time of 20 min. In another work by Sun et al. [23], it was shown that the obtained yield

* Corresponding author at: Chemical Engineering Department, Razi University, Taghe Bostan, Kermanshah, Iran. Tel.: +98 8314274530; fax: +98 8314274542.
E-mail addresses: masoudrahimi@yahoo.com, m.rahimi@razi.ac.ir (M. Rahimi).

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of methyl ester in microstructured reactors could be over 94% at the residence time of less than 1 min. The experiments took place with two different kinds of stainless steel capillary tube and a PTFE tube that connected to a micromixer. In another study, transesterification reaction of sunflower oil with ethanol in microreactors was investigated by Richard et al. [24]. They proposed a kinetics model under various ethanol to oil molar ratios and validated it with their measured values.

Many methods were employed to design the experiments and find out optimum condition in this process [25,26]. Among them, the response surface methodology is widely reported in literature. Somnuk et al. [27] reported continuous acid-catalyzed esterification of mixed crude palm oil using static mixer coupled with high-intensity ultrasonic irradiation. They used response surface methodology to optimize the two important reaction variables, methanol and sulfuric acid concentrations. Jaliliannosrati et al. [28] optimized biodiesel production from *Jatropha curcas L.* seed using response surface methodology. Response surface methodology (RSM) based on central composite design (CCD) was employed to analyze the influence of process variables on conversion of triglycerides in a batch process.

In the present study, a microreactor with T-shaped junction was used, as continuous flow reactor, for transesterification of soybean oil with methanol in presence of KOH. The influences the some process variables such as; KOH concentration, molar ratio of methanol to soybean oil, residence time and reaction temperature on transesterification of triglycerides was investigated. In addition, optimization study was carried using response surface methodology. The optimal transesterification conditions for producing the maximum methyl ester conversion and the relation between the parameters were determined using Box–Behnken experimental design method.

2. Materials and methods

2.1. Materials

Soybean oil was purchased from a local market and employed as feed for transesterification reactions. The additional materials used during synthesis were: methanol (99.5%, Merck), potassium hydroxide (85% pellets, Merck), hydrochloric acid (37%, Merck), normal hexane (GC grade, >99%, Merck). Methyl laurate (Methyl dodecanoate, 99.7%) was obtained from (Sigma) as standard for GC analysis. The Saponification index was (mg KOH/g oil) 191.88 and the mean molecular weight were calculated about 863.47 g/mol.

2.2. Methods and experimental procedure

Fig. 1 shows a schematic view of the microreactor rig. The microreactor included of a T-shaped plexiglass micromixer and a stainless steel microtube with an internal diameter of 0.8 mm. At first step, in order to prepare methanol solution, it is necessary the calculated amounts of catalyst and methanol were mixed together. The methanol/potassium hydroxide solution and oil were fed into two input channels of the studied T-micromixer by using a peristaltic pump (Qis™ DSP100). Both feeds mixed in the micromixer and passed through the microtube. The resistance time, the flow rates of the two feed streams and methanol solution/oil molar ratio were adjusted according to plan for experimental design.

The microreactor was immersed in a water bath to adjust the reaction temperature. The product was collected in a tank and for finishing the transesterification reaction, it was immersed in an ice-water bath. Consequently, it was reacted with hydrochloric acid to neutralize extra base catalyst. The collected produced in separation funnel was spited, into two phases, the FAME at the top and the glycerol at the bottom. Finally, the FAME phase was washed three times with distillated water at 80 °C for 5 min to remove residuals catalyst and glycerol.

The FAME contents in samples were analyzed by gas chromatography (Varian CP3800 Netherland), using a fused silica capillary column (DB-WAX, 30 m_250 lm_0.25 lm, nominal) and a flame ionization detector (FID). For this aim methyl laoranoate served as the internal standard for GC. The analysis of FAME wt% for samples was done by method of Wang et al. [29] according to the following equation:

$$\text{FAME}\ \% = \left(\frac{\text{area of all FAME}}{\text{area of all reference}} \times \frac{\text{weight of reference}}{\text{weight of biodiesel sample}}\right) \times 100$$

2.3. Design of experiments and optimization

Biodiesel production depends on various parameters. Therefore, in order to decrease the number of tests, it is necessary to employ design of the experiment (DOE) to reduce costs and economize the time. Response surface methodology and central composite design techniques have been reported in some research in literature for design and optimization of many processes [30–33].

In the present study, the Box–Behnken design was used to understand the effect of each variable on the continuous transesterification of soybean oil. Furthermore, using this technique it was tried to find optimum conditions and achieve the maximum biodiesel yield.

The factors selected for this optimization were KOH concentration, reactor temperature and molar ratio methanol to soybean oil. The range and levels of them are listed in Table 1 and the maximum values of the yield were taken as the responses in the experiment design.

Analysis of variance (ANOVA) is a reliable method to analyze and define the degree of certainty of experimental data [34]. Further statistical analysis of the model was performed to evaluate the ANOVA.

The response variable (FAME %) was fitted with a full quadratic model in order to relate the FAME % to these variables. The form of the mathematical model is shown in the Eq. (1):

$$Y_{yield} = \beta_0 + \sum_{i=1}^{3}\beta_i X_i + \sum_{i=1}^{3}\beta_{ii} X_i^2 + \sum_{i=1}^{2}\sum_{j=i+1}^{3}\beta_{ij} X_{ij} \quad (1)$$

where Y_{yield} is the FAME %, X_i and X_{ij} are the uncoded independent variables, β_0 is the offset term and β_i, β_{ii}, β_{ij} are regression coefficients.

3. Results and discussion

As discussed above, the operation conditions for the continuous production of biodiesel by microreactor are quite wide. Therefore, optimization of operational condition will be relatively important. In the following section, by using the Box–Behnken design of experiment, the effects of variables on the FAME % in the studied microreactor was explored. The corresponding Box–Behnken design, experimental data for FAME % at the design points are summarized in Table 2.

The effects of various operational parameters including; catalyst concentration, temperature and methanol/oil molar ratio on FAME % were studied. A residence time of 26 s was used, just as an example, for this analysis. In this reaction time, it was possible to see the effects of various operational parameters more clearly.